

AD-A116 560

POLYTECHNIC INST OF NEW YORK FARMINGDALE DEPT OF CHE--ETC F/6 20/8
MOLECULAR RELAXATION OF LITHIUM ARSENIC HEXAFLUORIDE IN ONE-TWO--ETC(U)

JUN 82 H FARBER, D IRISH, S PETRUCCI

DAA629-82-K-0048

UNCLASSIFIED

TR-1

ARO-18978.1-CH

ML

1...1
AD-2
16640

END
DATA
FILED
7-82
DTIC

AD A116560

ARO 18978.1-CH

(12)

MOLECULAR RELAXATION OF
LITHIUM ARSENIC HEXAFLUORIDE
IN ONE-TWO-DIMETHOXYETHANE

TECHNICAL REPORT #1

Herman Farber, Donald Irish and
Sergio Petrucci

June 30, 1982

U.S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

DAAG29/82/K/0048

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF NEW YORK
ROUTE 110
FARMINGDALE, LONG ISLAND, N.Y.

JPY
SILS
SILS

JUL 6 1982

A

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #1	2. GOVT ACCESSION NO. AD-A116360	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Molecular Relaxation of Lithium Arsenic Hexafluoride in One-Two-Dimethoxyethane	5. TYPE OF REPORT & PERIOD COVERED Technical Jan - June 1982	
7. AUTHOR(s) Herman Farber, Donald Irish and Sergio Petrucci	6. PERFORMING ORG. REPORT NUMBER DAAG29/82/K/0048	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Polytechnic Institute of New York; Route 110 Farmingdale, Long Island, New York 11735	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709	12. REPORT DATE June 30, 1982	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	13. NUMBER OF PAGES	
	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES THE VIEW, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS REPORT ARE THOSE OF THE AUTHOR(S) AND SHOULD NOT BE CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY OTHER DOCUMENTATION.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Electrical Conductance, Raman Spectra, Ultrasonic and Microwave Dielectric Relaxation of Lithium Arsenic Hexafluoride in 1-2 Dimethoxyethane ether.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) ✓ Audiofrequency electrical conductivity, Raman Spectra, radiofrequency ultrasonic absorption and microwave dielectric permittivity of LiAsF ₆ in the solvent 1-2 Dimethoxyethane (DME) are reported. Electrical conductivity reveal the electrolyte to be associated to ion-pairs (K _A = 1x10 ⁵ M ⁻¹). Raman Spectra of the symmetrical stretching mode		

of AsF_6^- suggest the ion to be "spectroscopically free", namely either unpaired or solvent separated from the cation.

Ultrasonic relaxation data are interpreted as due to the equilibrium $\text{Li}^+ + \text{S}, \text{AsF}_6^- \rightleftharpoons \text{LiAsF}_6$, S being a solvent molecule. The equilibrium appears to be heavily shifted toward the left, in accord with the information by Raman Spectra.

Microwave Dielectric Relaxation data can be interpreted as due to the diffusion rotational relaxation of ion - pairs. Estimate of the charge to charge distance in the rotating pairs reinforces the notion that the solvent resides between the cation and the anion in the majority of the pairs. Mass Law appears to shift the equilibrium toward the contact pairs, by increasing the electrolyte concentrations.

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

Accession No.	
NTIS GRA&I	
REF ID: TAB	
UNCLASSIFIED	
DATE 10/10/88	



A

Molecular Relaxation of LiAsF₆ in
1-2 Dimethoxyethane

by

Herman Farber, Donald E. Irish⁰
and Sergio Petrucci

Depts. of Electrical Engineering and
Chemistry, Polytechnic Institute of
New York, Farmingdale Campus
Route 110, Farmingdale, Long Island N.Y.

Abstract

Audiofrequency electrical conductivity, Raman spectra, radiofrequency ultrasonic absorption and microwave dielectric permittivity of LiAsF₆ in the solvent 1-2 Dimethoxyethane (DME) are reported.

Electrical conductivity reveal the electrolyte to be associated to ion-pairs ($K_A = 1 \times 10^5 \text{ M}^{-1}$). Raman spectra of the symmetrical stretching mode of AsF₆⁻ suggest the ion to be "spectroscopically free", namely either unpaired or solvent separated from the cation.

Ultrasonic relaxation data are interpreted as due to the equilibrium $\text{Li}^+, \text{S}, \text{AsF}_6^- \rightleftharpoons \text{LiAsF}_6$, S being a solvent molecule. The equilibrium appears to be heavily shifted toward the left, in accord with the information by Raman spectra.

Microwave Dielectric Relaxation data can be interpreted as due to the diffusion rotational relaxation of ion-pairs.

Estimate of the charge to charge distance in the ion - pairs reinforces the notion that the solvent resides between the cation and the anion in the majority of the pairs. Mass Law appears to shift the equilibrium toward the contact pairs, by increasing the electrolyte concentrations.

Introduction

Progress in lithium batteries, using lithium electrolytes in ethereal solutions, has occurred largely in the last decade. Some battery systems have been recorded as being able to be recycled several hundred times.^{1,2}

Still many problems persist³ which make further studies of the molecular properties of lithium electrolytes quite relevant both on theoretical and practical grounds.

LiClO_4 as electrolyte in THF⁴ was studied by us years ago by ultrasonic relaxation methods. Later we extended our study to 1-2 DME⁵ because of its ability to chelate alkali - ions.

We decided then to start a research program on similar lines of the electrolyte LiAsF_6 which, in preliminary tests, appears more ionized than LiClO_4 in ethereal solvents.

Our aim is to try to give, by a diversified study by classical and modern methods, a molecular picture of the particular behavior of a given electrolyte as LiAsF_6 in a given ether. Hopefully this would give a molecular rationale for the choice of a given electrolyte in battery construction. Empiricism on the contrary and phenomenological information (low internal resistance) has been the criteria so far in the majority of the cases.

Experimental Part

The experiment and procedure for the conductivity, ultrasonic and dielectric measurements have been described elsewhere.^{5,6}

Raman spectra were collected at the University of Waterloo, Ontario Canada from a Jarrel-Ash 100 Raman spectrometer equipped with an argon-ion laser source tuned at 514.5 nm and interfaced to a Commodore microcomputer.

1-2 Dimethoxyethane was purified as described before.⁵ LiAsF₆ (Alfa Division, Andover Mass.) was redried in vacuum at 60°C for one day. The original product was found, by weight loss, to contain about 1% of moisture. Raman spectra of solutions prepared using the original product, revealed a faint OH stretch band at about 3500 cm⁻¹, the same position 3520 cm⁻¹ shown by a 0.4 M aqueous solution in 1-2 DME prepared and used for comparison's sake. The distilled solvent had no water band in the same wavelength region. Solutions at comparable concentrations of the dried LiAsF₆ in 1-2 DME showed no water band by Raman spectra.

Repetitive attempts to dry LiAsF₆ in vacuum at 100 - 115°C resulted in the same weight loss as above. However when the dried product was dissolved in 1-2 DME, some opalescence and small amounts of precipitate occurred, suggesting some thermal decomposition of the electrolyte, upon drying at 100 - 115°C. Solutions were prepared by weight for the conductance runs, converting the molalities to molarities by the use of densities. Other solutions were prepared weighing the electrolyte directly in volumetric flasks and diluting to mark with the distilled solvent. All the solutions were used shortly after preparations and kept sealed in large dessicators over Mg(ClO₄)₂. Contact with the

open air in transferring the solutions to the cells or capillaries
was kept within 30 - 60 seconds.

Results and Calculations

(Fig.1A) Fig. 1A shows the equivalent conductance data $\Lambda(\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1})$ plotted vs. the concentration c (mole/liter = M) in a log-log plot, for LiAsF_6 in 1-2 DME at $t = 25.00^\circ\text{C}$. In the same plot the corresponding data for LiClO_4 are reported.⁵ One may see that there is a dramatic increase of almost one order of magnitude in the equivalent conductance of the LiAsF_6 with respect to the one of LiClO_4 in 1-2 DME. Fig. 1B shows the Fuoss-Kraus⁷ plot of $\Lambda\sqrt{c}$ vs. c according to the simplified version of the triple - ion theory, neglecting long range ionic interactions. A curvature appears in the plot as already noticed for LiClO_4 in 1-2 DME⁵. By applying linear regressions one obtains determination coefficient $r^2 = 0.983$; Intercept = 0.558; Slope = 65.5. This simplified theory leads to:

$$\Lambda\sqrt{c} = \frac{\Lambda_0}{\sqrt{K_A}} + \frac{K_T \Lambda_0^T}{\sqrt{K_A}} c, \quad (I)$$

with K_A and K_T the ion - pair and triple ion formation constants [using the symmetrical approximations $K_{T1} = K_{T2}$ for the two possible triple ions $\text{Li}(\text{AsF}_6)_2^-$ and $\text{Li}_2(\text{AsF}_6)^+$].⁷ Further Λ_0^T is the triple ion conductance set equal to $2/3\Lambda_0$.⁸ We have evaluated Λ_0 from Walden's rule and the figure $\Lambda_0(\text{LiAsF}_6) = 178.2 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ in CH_3CN at 25°C .⁹ The viscosity of acetonitrile at 25°C is $\eta = 0.003449$ poise¹⁰ which gives $\Lambda_0\eta = 0.615$ in acetonitrile. The viscosity of 1-2 DME is $\eta = 0.004129$ poise.¹¹ Therefore from Walden's rule we calculate $\Lambda_0(\text{LiAsF}_6) = 149 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$ in 1-2 DME at 25°C . From the above data one then calculates $K_A = 0.71 \times 10^5 \text{ M}^{-1}$ and $K_T = 177 \text{ M}^{-1}$. Presence of the curvature and suspect of large systematic errors involved in neglecting interionic terms led us to

the use of the full version of the Fuoss - Kraus theory.⁷ This gives:

$$\Lambda g(c) \sqrt{c} = \frac{\Lambda_0}{\sqrt{K_A}} + \frac{\Lambda_0^T K_T}{\sqrt{K_A}} c \left(1 - \frac{\Lambda}{\Lambda_0}\right), \quad (II)$$

$$\text{with}^{5,7} g(c) = \frac{\exp \left(- \frac{\beta'}{\sqrt{\Lambda_0}} \sqrt{c\Lambda} \right)}{\left(1 - \frac{S}{\Lambda_0^{3/2}} \sqrt{c\Lambda} \right) \left(1 - \frac{\Lambda}{\Lambda_0} \right)^{1/2}} \quad (III)$$

β' is the Debye - Hückel activity coefficient and S the Onsager conductance coefficient.

(Fig.1C) A plot of eq. II is shown in Fig. 1C. The curvature is largely disappeared. Linear regressions give: $r^2 = 0.973$; Intercept = 0.464; Slope = 8.545. From this $K_A = 1.0 \times 10^5 \text{ M}^{-1}$ and $K_T = 28 \text{ M}^{-1}$. As in previous cases,¹² some change in K_A but a huge variation in K_T' are noticed. We believe the latter figure $K_T = 28 \text{ M}^{-1}$ to be more reliable. Notice that for LiClO_4 in 1-2 DME at 25°C we calculated⁵ $K_A = 4.1 \times 10^6 \text{ M}^{-1}$ and $K_T = 20.3 \text{ M}^{-1}$. This indicates that the increase in conductivity of LiAsF_6 with respect to LiClO_4 is mainly due to a decrease of ion -

(Fig.2) pair association by one order of magnitude. Fig. 2 shows the Raman spectra of LiAsF_6 0.4 M and 0.2 M corresponding to the symmetrical stretch of AsF_6^- ion.¹³ No asymmetry of the spectrum is visible.

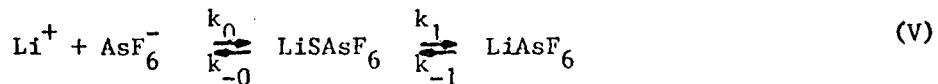
This suggests that AsF_6^- is spectroscopically free, namely not in contact with Li^+ . Because of the above conductance information ($K_T = 10^5 \text{ M}^{-1}$), the logical conclusion is that Li^+ must seat in the majority of the cases around AsF_6^- but separated by one or more solvent molecules. It appears therefore that a preponderant portion of the ion - pairs exists as solvent separated pairs.

(Fig. 3A) Fig. 3A and 3B shows the ultrasonic spectrum of LiAsF_6 in 1-2 DME at (& 3B) various concentrations and temperatures in the form of α/f^2 vs. f , where α is the absorption coefficient of sound (neper cm^{-1}) and f the frequency. The solid fitted lines are the Debye function for a single relaxation function:

$$\frac{\alpha}{f^2} = \frac{A}{1 + (f/f_r)^2} + B, \quad (\text{IV})$$

where A is a relaxation parameter, f_r is the relaxation frequency and B the background sound absorption at $f \gg f_r$. The results for A , f_r and B together with the sound velocities U (cm s^{-1}) and the calculated maximum excess sound absorption per wavelength (Table I) μ_m ($= 1/2 A f_r U$) are collected in table I.

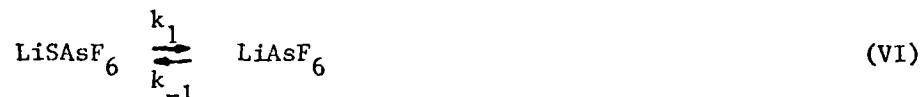
From table I it is apparent that at 25°C f_r is independent of concentration within experimental error ($\pm 5\%$). Further μ_m is linear with c (see below). These observations suggest a first order or pseudo - first order process of the type $\text{A} \rightleftharpoons \text{B}$. From the information above we advance the hypothesis that the process of ionic association between Li^+ and AsF_6^- follows the Eigen - type mechanisms:



followed by further steps leading to triple ions. However we are dis-
regarding these further steps for the treatment of the ultrasonic process.
Formation of triple ions would require at least a second order process
and a concentration dependent relaxation frequency contrary to what

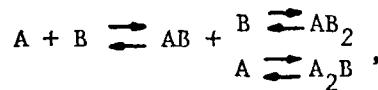
observed here.

Because of the value of $K_A = 1 \times 10^5 \text{ M}^{-1}$, we suggest that at the concentrations of the ultrasonic work the first step of scheme V is irrelevant, too few free ions existing. The process then may be written as:



We will denote the free ion concentrations by c_1 and the ones of the two complex species by c_2 and c_3 respectively, with the condition $c \approx c_1 + c_2 + c_3$ (neglecting other species).

This approximation may be justified as follows: Given the scheme⁷:



$$(\text{AB}) = (1 - \alpha - 3\alpha_T)c \approx c; (\text{A}) = (\text{B}) = \alpha c; (\text{AB}_2) = (\text{A}_2\text{B}) = \alpha_T c$$

Then:

$$K_A = \frac{1-\alpha}{\alpha^2 c} = \frac{1}{c}; \alpha = \sqrt{K_A} \sqrt{c},$$

$$K_T = \frac{\alpha_T}{\alpha c (1 - \alpha - 3\alpha_T)} \approx \frac{\alpha_T}{\alpha c}; \alpha_T = \sqrt{\frac{K_T}{K_A}} \sqrt{c}.$$

If $K_T = 28 \text{ M}^{-1}$ and $K_A = 1 \times 10^5$ at $c = 0.1 \text{ M}$, $\alpha_T = 0.03$, $\alpha_T c = (\text{AB}_2) = (\text{A}_2\text{B}) = 3 \times 10^{-3} \text{ M}$. Further $\alpha = 0.01$ and single ions account only for a few percent of the total concentration of electrolyte (neglecting other species).

The collected data of Table I applied to scheme VI lead to the following treatment.

From the relation:¹⁴

$$\tau^{-1} = k_1 + k_{-1} = k_{-1}(1 + K_1) = \frac{kT}{h} e^{-\frac{\Delta S_{\neq 1}}{R}} e^{-\frac{\Delta H_{\neq 1}}{RT}} (1 + K_1), \quad (VII)$$

a plot of $\ln(\tau^{-1}/T)$ vs. $(1/T)$ should be linear with slope and intercept:

$$\text{Slope} = \frac{d \ln(\tau^{-1}/T)}{d(1/T)} = -\frac{\Delta H_{\neq 1}}{R} - \frac{K_1}{1+K_1} \frac{\Delta H_1}{R}, \quad (VIII)$$

$$\text{Intercept} = \left(\ln\left(\frac{k}{h}\right) + \frac{\Delta S_{\neq 1}}{R} \right). \quad (IX)$$

(Fig. 4A) The results are shown in Fig. 4A. The solid line has been calculated by linear regressions. The results are: $r^2 = 0.995$, Intercept = 22.74, and Slope = -2510. From the intercept one calculates $\Delta S_{\neq 1} = -2.0$ e.u. Scheme VI leads also to the relation:¹⁴

$$\mu_m = \frac{\pi}{2\beta_s} \frac{(\Delta V_s)^2}{RT} \frac{K_1}{(1+K_1)^2} c, \quad (X)$$

Where the isentropic compressibility $\beta_s = \frac{1}{\rho U^2}$ and $\Delta V_s = \Delta V_T - \frac{\theta_p}{\rho c_p} \Delta H_1$, with θ_p the expansivity ρ the density, c_p the specific heat of the liquid.

Eq. X implies that a plot of $\ln(\mu_m T/U^2)$ vs. $1/T$ should give a straight line with slope:¹⁴

$$\frac{d \ln(\mu_m T/U^2)}{d(1/T)} = \frac{K_1 - 1}{K_1 + 1} \frac{\Delta H_1}{R} \quad (XI)$$

(neglecting the temp. dependence of ρ and c_p).

(Fig. 4B) The results are shown in Fig. 4B. Linear regressions applied to these

data give: $r^2 = 0.991$, Intercept = -14.82, and Slope = -2517.

We are now able to write the system of three equations:¹⁴

$$\left\{ \begin{array}{l} \frac{d \ln(\tau^{-1}/T)}{d(1/T)} = -2510 = -\frac{\Delta H_{-1}^{\neq}}{R} - \frac{K_1}{1+K_1} \frac{\Delta H_1}{R}, \\ \frac{d \ln(\mu_m T/U^2)}{d(1/T)} = -2517 = \frac{K_1 - 1}{K_1 + 1} \frac{\Delta H_1}{R}, \\ \tau^{-1} = \frac{kT}{h} e^{\Delta S_{-1}^{\neq}/R} e^{-\Delta H_{-1}^{\neq}/RT} (1 + K_1), \end{array} \right.$$

with the unknown parameters K_1 , ΔH_1 , ΔH_{-1}^{\neq}

Trial and errors by changing K_1 lead to compatible solutions with $K_1 \approx 0.01$ (K_1 much smaller than 10^{-2} gives still compatible solutions but it is unreasonable. No ultrasonic relaxation would be observable if the concentration of one of the two species is too small).

The final results then are:

$$K_{-1} \approx 10^{-2} \text{ i.e. } k_{-1} \gg k_1 ,$$

$$\tau^{-1} \approx k_1 = 5.0 \times 10^8 \text{ s}^{-1} ,$$

$$\Delta H_{-1}^{\neq} = 4.9 \text{ Kcal/mole} ,$$

$$\Delta S_{-1}^{\neq} = -2.0 \text{ e.u.} ,$$

$$\Delta H_1 = 5.1 \text{ Kcal/mole} ,$$

$$\Delta H_1^{\neq} = 10.0 \text{ Kcal/mole} ,$$

Further information can be obtained as follows:

If $K_1 = 10^{-2}$, $\Delta G_1 = -RT \ln K_1 = 2.73 \text{ Kcal/mole}$, and $\Delta S_1 = \frac{1}{T}(\Delta H_1 - \Delta G_1) = 8.0 \text{ e.u.}$

Then: $\Delta S_1^{\neq} = \Delta S_1 + \Delta S_{-1}^{\neq} = 6.0 \text{ e.u.}$ and $k_{-1} = 6 \times 10^6$.

Finally, combination of ultrasonic and conductance results lead to the correlation:

$$K_A = 1.0 \times 10^5 = K_0(1 + K_1) \approx K_0 \quad \text{as } K_1 = \frac{c_3}{c_2} = 0.01.$$

This implies that $c_3 \ll c_2$ and that the contact species are in much smaller concentrations than the solvent separated species. Notice that calling $\frac{c_3}{c_2} = 0.01$ would imply the converse condition at variance with the indication by Raman spectra.

[The ultrasonic relaxation method cannot indicate for a first order process the direction of the molecular process which must be deduced from collateral information.]

If the above is correct, it would imply that we are looking for the observed process $\tau^{-1} = k_{-1}$, to the transformation $c_3 \rightleftharpoons c_2$.
or $\text{LiAsF}_6 \rightleftharpoons \text{LiSAsF}_6$. A final parameter can be calculated.

From eq. X one would expect linearity between μ_m and c . This is shown (Fig. 4C) in Fig. 4C. Linear regressions, forcing the intercept through the origin, (50% statistical weight to the origin), gives: $r^2 = 0.986$, Slope = 12.0, by expressing c in mole/cm³. Then since $K_1 \ll 1$:

$$\Delta V_S = \left[\frac{2\beta_S RT}{\pi K_1} \frac{\mu_m}{c} \right]^{1/2} = 40.4 \text{ cm}^3/\text{mole}.$$

(Fig. 5A) Fig. 5A shows ϵ' and $(\epsilon'' - \epsilon''_x)$, the coefficients of the real and imaginary parts of the complex permittivity $\epsilon^* = \epsilon' - J(\epsilon'' - \epsilon''_x)$ plotted vs. the frequency f (GHz) for a representative concentration of LiAsF_6 in 1-2 DME. The frequency covered is $\sim 1 - 90$ GHz. The solid lines are the sum of two single Debye processes according to the functions:

$$\epsilon' = \frac{(\epsilon_0 - \epsilon_{\infty 1})}{1 + (f/f_{r1})^2} + \frac{(\epsilon_{\infty 1} - \epsilon_{\infty 2})}{1 + (f/f_{r2})^2} + \epsilon_{\infty 3}; \quad (\text{XII})$$

and:

$$\epsilon'' - \epsilon''_x = (\epsilon_0 - \epsilon_{\infty 1}) \frac{f/f_{r1}}{1 + (f/f_{r1})^2} + (\epsilon_{\infty 1} - \epsilon_{\infty 2}) \frac{f/f_{r2}}{1 + (f/f_{r2})^2}, \quad (\text{XIII})$$

where $\epsilon''_x = \frac{1.8 \times 10^{12} x}{f}$ is the specific conductance contribution to the dielectric loss; x is the specific conductance and ϵ_0 is the static permittivity of the solution. The quantities ϵ_0 , $\epsilon_{\infty 1}$, f_{r1} are due to the presence of the solute whereas the parameters $\epsilon_{\infty 2}$ and f_{r2} are relaxation parameters of the solvent in the solution. In other words the pure solvent would have similar values of $\epsilon_0^{\text{solvent}} = \epsilon_{\infty 1}$, $\epsilon_{\infty 2}$ and f_{r2} as for the solutes, at least in dilute solutions.

The dashed lines in Fig. 5A are the single Debye contributions to $\epsilon'' - \epsilon''_x$.

(Fig. 5B) Fig. 5B reports the Cole - Cole plot $\epsilon'' - \epsilon''_x$ vs. ϵ' for the same solution of LiAsF_6 in 1-2 DME. The solid line is the sum of the two individual Debye contributors indicated in Fig. 5B by the dashed semicircles. The parameters ϵ_0 , $\epsilon_{\infty 1}$, $\epsilon_{\infty 2}$, f_{r1} and f_{r2} , together with the conductance of the (Table II) solutions studied, is reported in Table II.

Discussion

Conductance, Raman spectra and ultrasonic relaxation all concur to suggest that the majority of LiAsF_6 exists as an outer - sphere or solvent - separated ion - pair.

Fig. 6 shows the relaxation strength $(\epsilon_0 - \epsilon_{\infty 1})$ plotted vs. the concentration $c \approx c_2$ for LiAsF_6 in 1-2 DME.

According to the Böttcher equations:¹⁵

$$\epsilon_0 - \epsilon_{\infty 1} = \frac{4\pi L c \times 10^{-3}}{(1 - \alpha f)^2} \frac{\mu^2}{3kT} \frac{3\epsilon_0}{2\epsilon_0 + 1} c . \quad (\text{XIV})$$

By neglecting the polarizability - reaction field factor $(1 - \alpha f)^2$ (generally of the order of 0.9), one can calculate μ . Linear regressions analysis applied to the data of Fig. 6, forcing the intercept through the origin gives:

$$r^2 = 0.999, \text{ Slope} = 19.8 \times 10^3$$

where c has been expressed in mole/cm³.

It results $\mu = 18.0 \times 10^{-18}$ e.s.u. cm. By taking a rigid sphere model it results $\mu = ea$, where e is the charge of the electron. Then $a = 3.8 \times 10^{-8}$ cm the apparent charge to charge separation of the Li^+ and AsF_6^- in the rotating dipole.

Notice that, from conductance $K_1 \approx K_0 = 1 \times 10^5 \text{ M}^{-1}$. By equating K_0 to the Fuoss - Jagodzinski equation:⁴

$$K_0 = K_F = \frac{4\pi La^3}{3000} e^{-1/2} e^b, \quad (\text{XV})$$

$$\text{with } b = \frac{e^2}{a c k T}$$

on can evaluate $a \approx 6.3 \times 10^{-8}$ cm, a figure larger than the value estimated above from the dielectric data. This might be due to the mass effect and to the higher concentration used in the dielectric work, forcing more contact species to be present. This would lower the average distance between the ions in the pairs.

References

0. Dept. of Chemistry, Univ. of Waterloo, Ontario, Canada
1. Gaines L. H., Francis R. W., Newman G. H., Rao B. M. L.
Proc. 11th IECE Conference, Stateline, NV (1976)
2. Newman G. H., Workshop on Lithium non - aqueous
Battery Electrochemistry June 4 - 6 (1980) Case Inst. of Technology,
Cleveland, Ohio
3. Goldman J. L., Mank R. M., Young J. H., Koch V. R.
J. Electrochem Soc. (1980) 127,1461
4. Jagodzinski P., Petrucci S. J. Phys. Chem. (1974) 78,917
5. Onishi S., Farber H., Petrucci S. J. Phys. Chem. (1980) 84,2922
6. Farber H., Petrucci S. J. Phys. Chem. (1975) 79,1221
Saar D., Brauner J., Farber H., Petrucci S. J. Phys. Chem. (1978) 82,545
7. Fuoss R. M., Accascina F. "Electrolyte Conductance" Interscience. NY (1959)
8. Boileau S., Emery P. Electroch. Acta (1976) 21,647
9. Hopkins H. P. Jr., Jahagirdar D. V., Norman A. B. J. Sol. Chem.
(1979) 8,147
10. Berns D. S., Fuoss R. M., J. Am. Chem. Soc. (1960) 82,5585
11. Saar D., Brauner J., Farber H., Petrucci S. Adva. Mol. Rel. Proc.
(1980) 16,263
12. Farber H., Petrucci S., J. Phys. Chem. (1981) 85,2987
- 13.
14. Chen C., Petrucci S., J. Phys. Chem., in press July (1982)
15. Bottcher C. F. J. "Theory of Electric Polarization" Elsevier, Amsterdam 1973

TABLE I

Ultrasonic relaxation parameters A, B, and f_r , sound velocity U and maximum excess absorption per wavelength μ_m for LiAsF_6 in 1-2 DME at the concentrations c and temperatures investigated.

t (°C)	c (M)	$A \times 10^{17}$ ($\text{cm}^{-1} \text{s}^2$)	$B \times 10^{17}$ ($\text{cm}^{-1} \text{s}^2$)	f_r (MHz)	$U \times 10^{-5}$ (cm s^{-1})	$\mu_m \times 10^5$ -----
1.0	0.30	102	60	35	1.286	230
10.0	0.29	95	55	48	1.248	285
15.0	0.30	88	55	55	1.233	299
25.0	0.40	95	55	80	1.209	459
25.0	0.30	80	51	80	1.181	378
25.0	0.20	64	48	80	1.123	287
25.0	1.10	35	43	80	1.130	158

TABLE II

Dielectric Relaxation Parameters ϵ_0 , $\epsilon_{\infty 1}$, $\epsilon_{\infty 2}$, f_{r1} , f_{r2} and specific conductance x of LiAsF_6 in 1-2 DME at the concentrations investigated at $t = 25^\circ\text{C}$.

c (M)	ϵ_0	$\epsilon_{\infty 1}$	$\epsilon_{\infty 2}$	f_{r1} (MHz)	f_{r2} (MHz)	x $\Omega^{-1} \text{cm}^{-1}$
0.10	9.8	7.0	2.7	2.0	35	1.4×10^{-3}
0.05	8.7	7.2	2.9	2.0	30	7.3×10^{-4}
0.028	8.0	7.2	3.0	2.0	35	3.5×10^{-4}

Captions for the figures

Fig. 1 A $\log \Lambda$ vs. $\log c$ for LiAsF_6 and LiClO_4 in 1-2 DME at $t = 25^\circ\text{C}$

B $\Lambda\sqrt{c}$ vs. c for LiAsF_6 in 1-2 DME; $t = 25^\circ\text{C}$

C $\Lambda g(c)\sqrt{c}$ vs. $c(1 - \frac{\Lambda}{\Lambda_0})$ for LiAsF_6 in 1-2 DME; $t = 25^\circ\text{C}$

Fig. 2 Raman Spectrum of LiAsF_6 0.2 M and 0.4 M in 1-2 DME in the symmetrical stretch region of AsF_6^-

Fig. 3 A - C (α/f^2) vs. frequency f for LiAsF_6 in 1-2 DME at various concentrations at $t = 25^\circ\text{C}$

B (α/f^2) vs. frequency f for LiAsF_6 0.3 M in 1-2 DME at $t = 10^\circ\text{C}$

Fig. 4 A Eyring plot: $\ln(\tau^{-1}/T)$ vs. $1/T$ for LiAsF_6 0.3 M in 1-2 DME

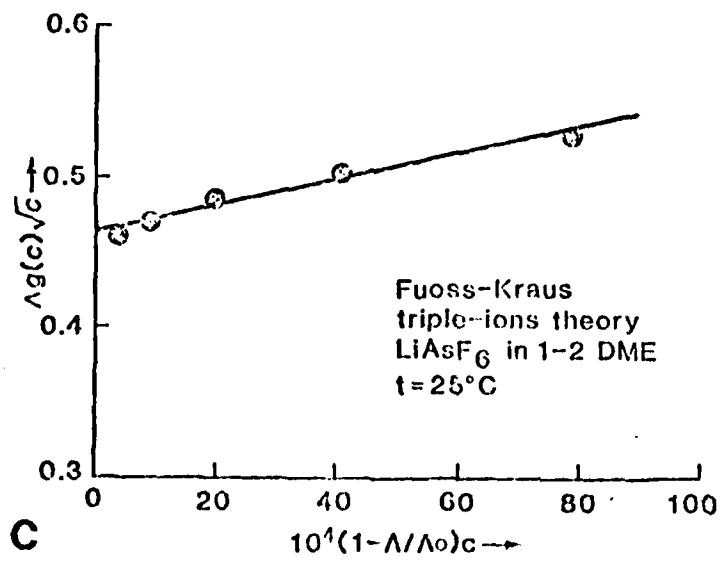
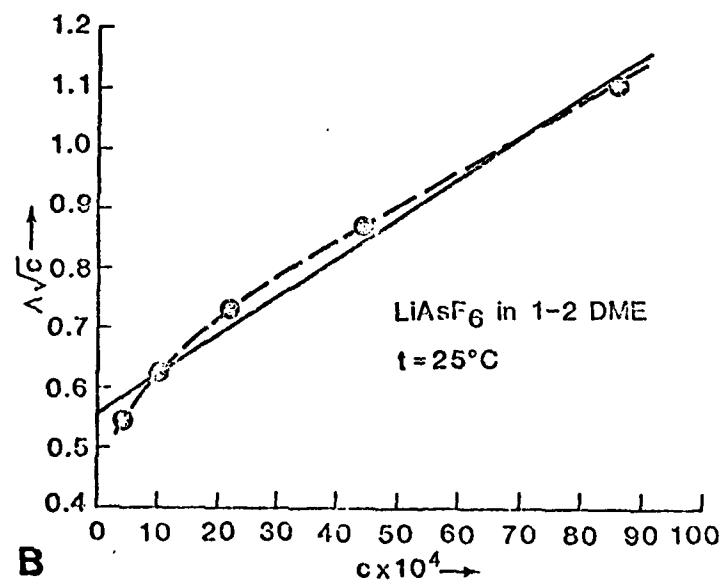
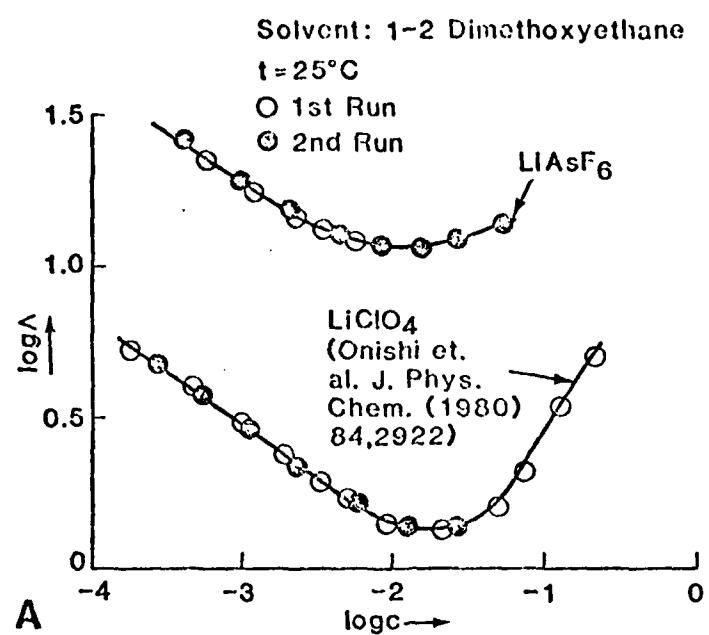
B Lamb plot: $\ln(\mu_m T/U^2)$ vs. $1/T$ for LiAsF_6 0.3 M in 1-2 DME

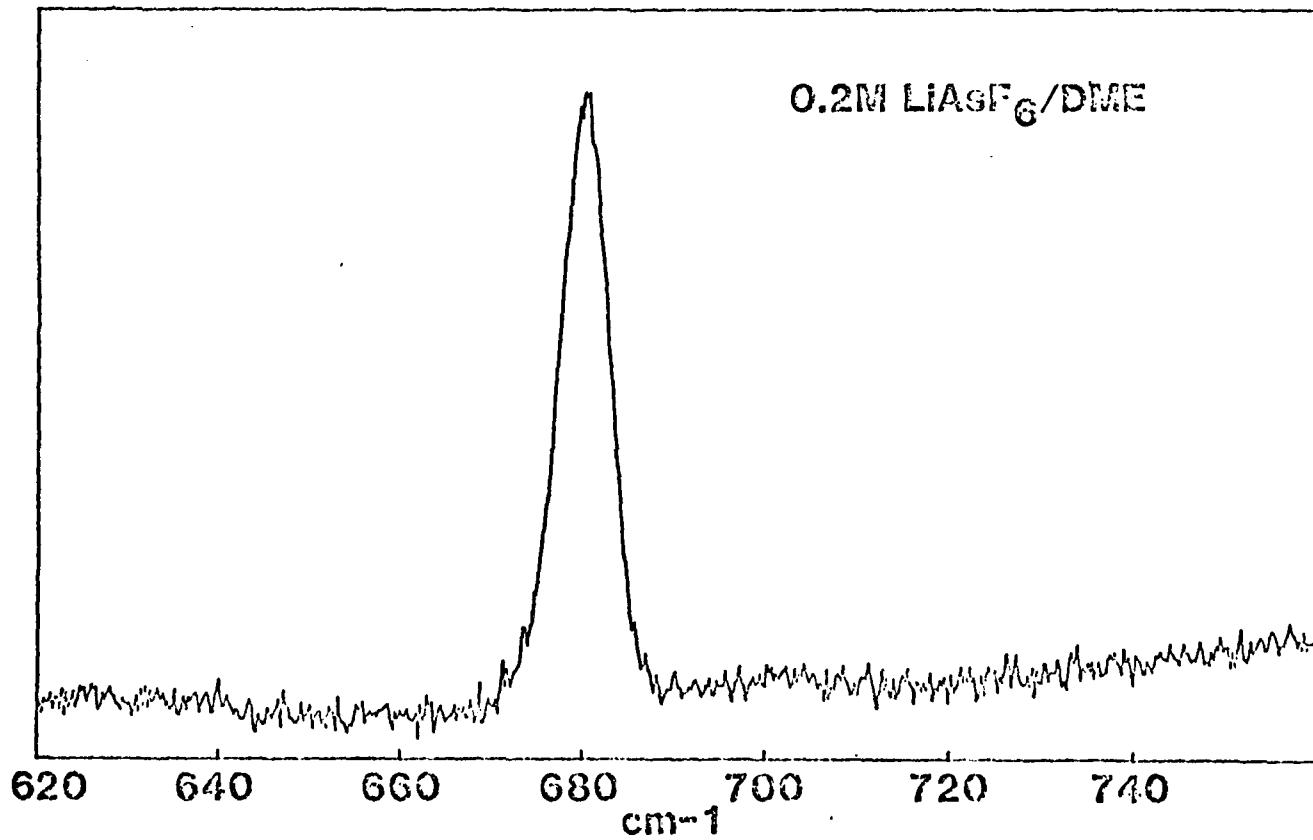
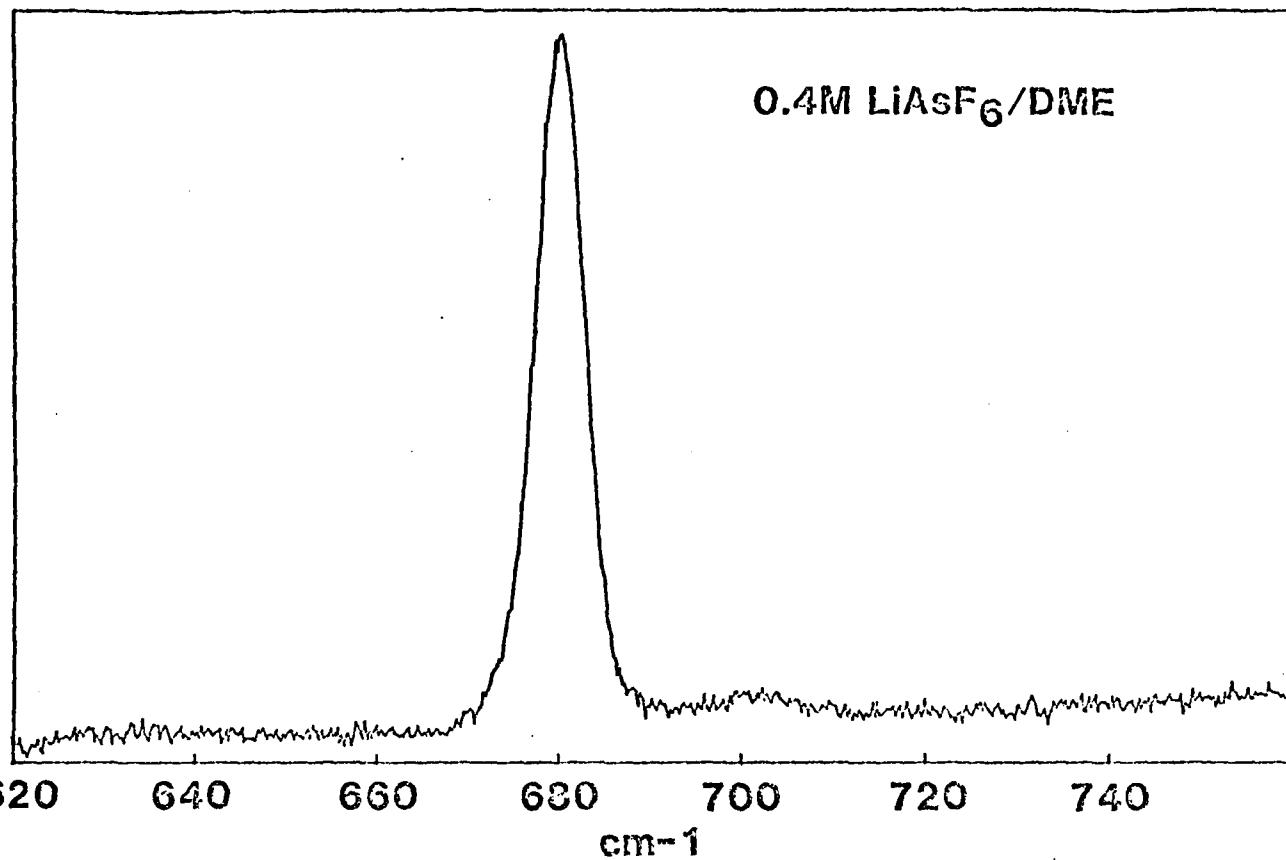
C μ_m vs. concentration for LiAsF_6 in 1-2 DME; $t = 25^\circ\text{C}$

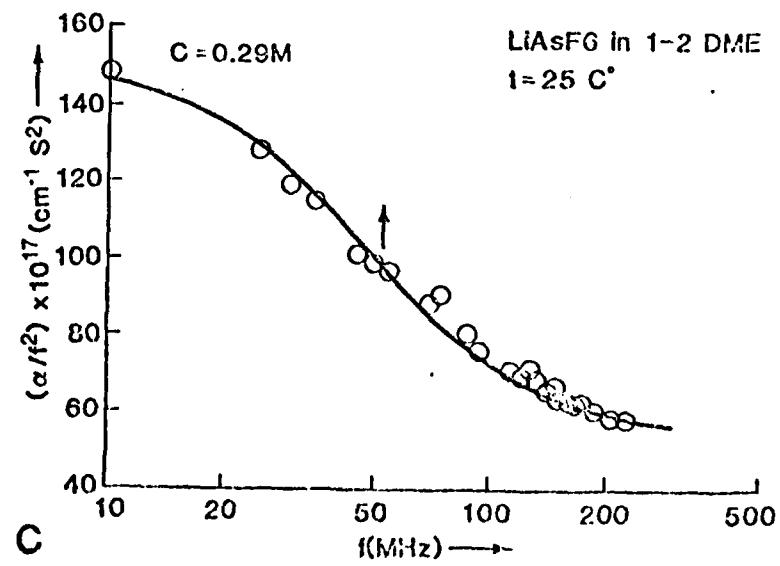
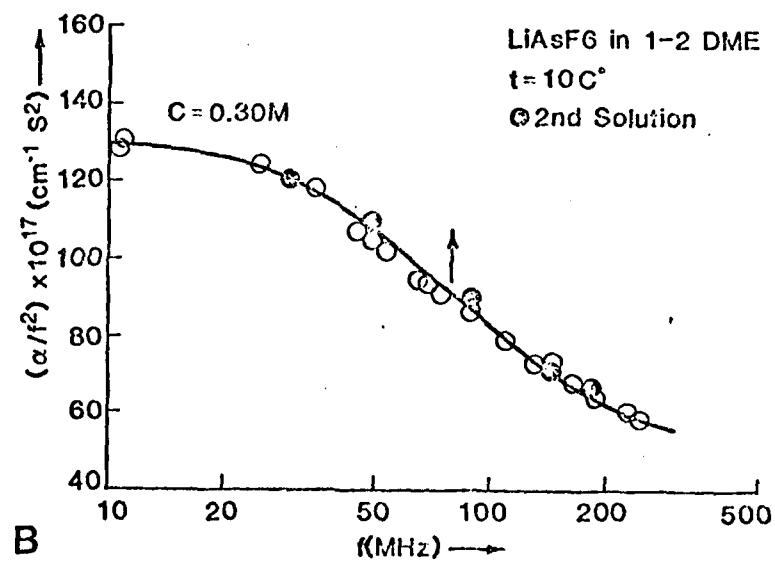
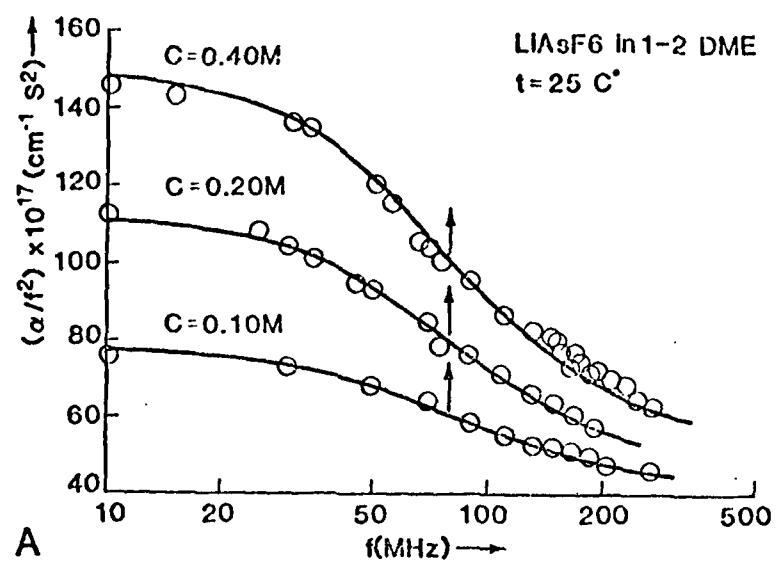
Fig. 5 A ϵ' and $(\epsilon'' - \epsilon''_x)$ vs. frequency f for LiAsF_6 0.05 M in 1-2 DME at $t = 25^\circ\text{C}$

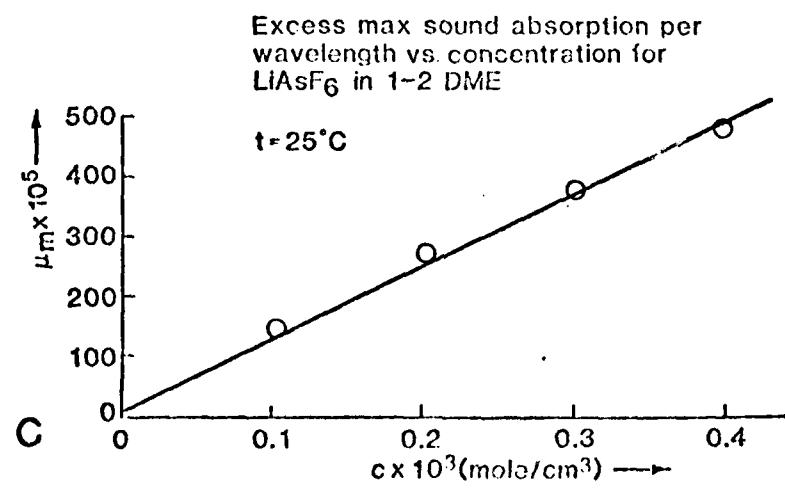
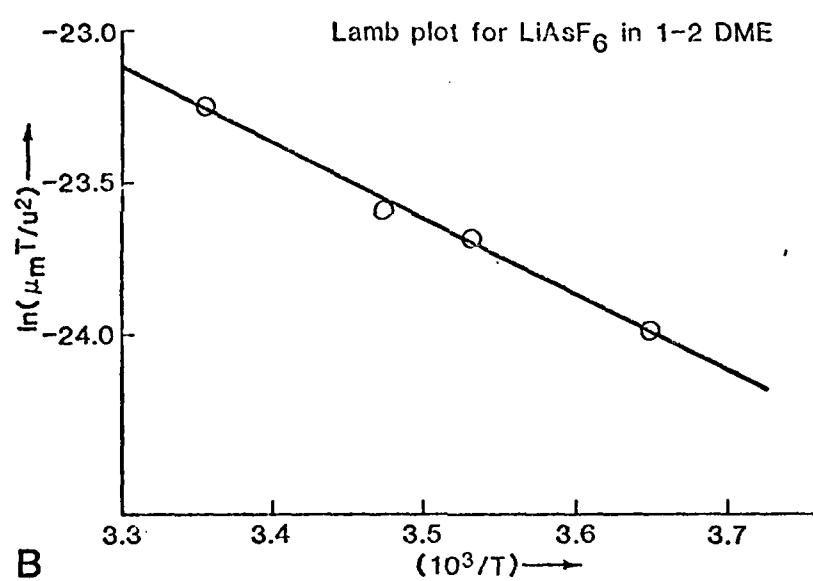
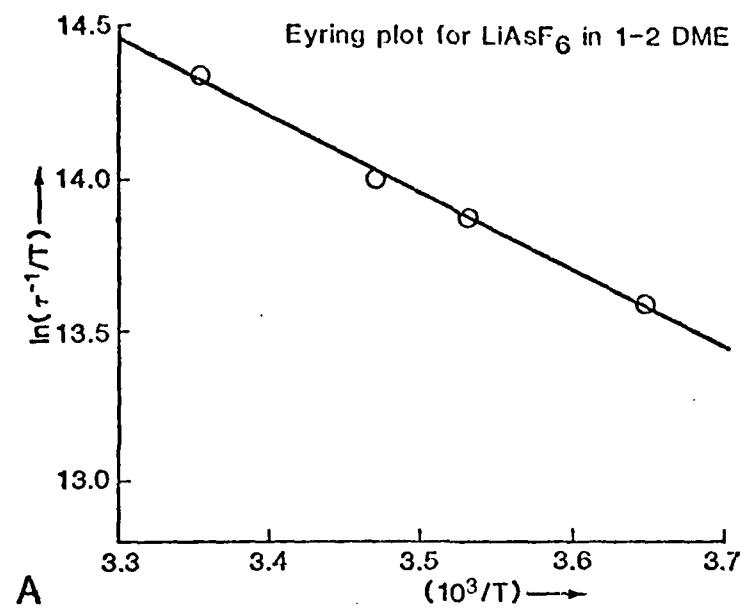
B $(\epsilon_0 - \epsilon_{\infty 1})$ vs. concentration c for LiAsF_6 in 1-2 DME at $t = 25^\circ\text{C}$

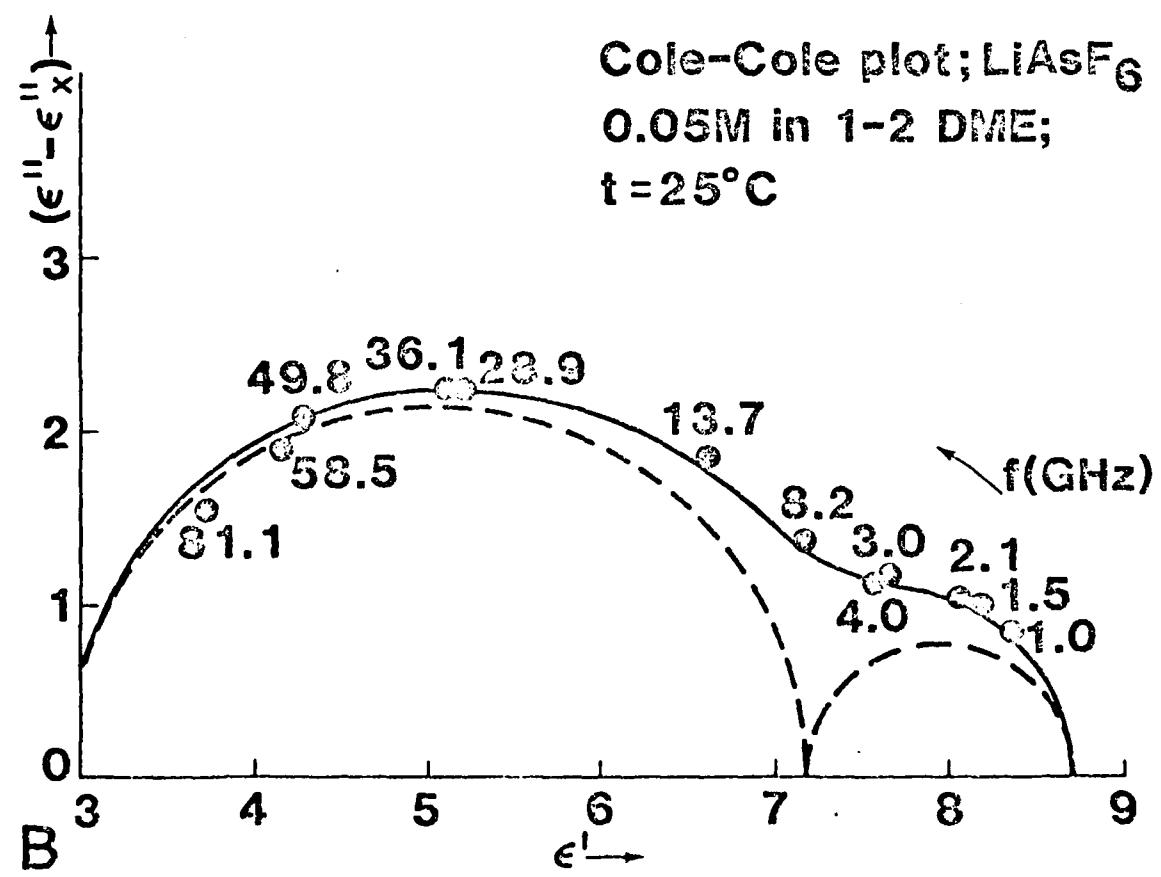
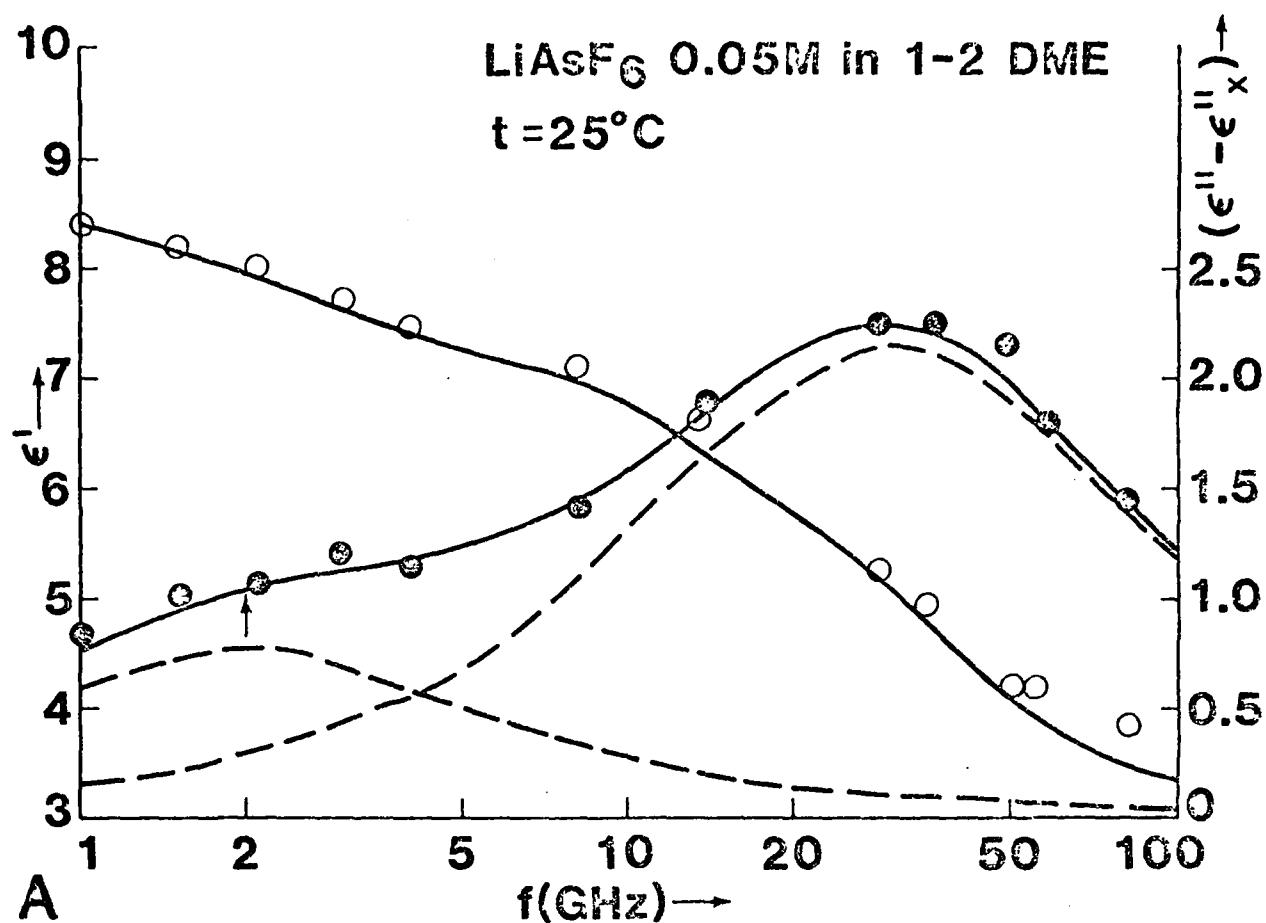
Fig. 6 Böttcher equation for LiAsF_6 in 1-2 DME











Böttcher's equation:
 $[(\epsilon_0 - \epsilon_{001})(2\epsilon_0 + 1/3\epsilon_0)]$
vs concentration for
LiAsF₆ in 1-2 DME
 $t = 25^\circ\text{C}$

